



## Actinide Speciation in the Presence of Humic Substances in Natural Water Conditions

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### Abstract

A review of literature data concerning complex properties of humic substances with actinides (Th, U, Np, Pu, Am) and with cations largely present in natural waters is presented. From data which have been selected according to criteria discussed in the present paper, speciation diagrams of actinides have been calculated in the most representative conditions for natural systems (pH range 4–9; [humic substances] 0.1 to 10 ppm). Humic substances dominate actinide (Th, U, Am) speciation up to pH 7 (or even 8). Above these pH, inorganic complexes regulate actinide speciation. The presence of competing cations (Ca or Al) modifies actinide speciation in the pH range 4–6.

### Introduction

The determination of radioelement speciation in natural waters is of prime importance for the safety assessment of radioactive waste disposal in geological formations. As emphasized in the literature [1–3], complex formation with ligands present in natural aquifers (ground or surface waters) may significantly influence the migration behaviour of radioelements, in particular complexation of radionuclides with natural organic ligands such as humic substances. A detailed knowledge of radioelement speciation in their presence necessitates the determination of the formation constants of the complexes. Due to the complex and heterogeneous nature of humic substances [1, 4], the determination of such data is relatively difficult and leads to a dispersity of values as well as discrepancies between them. A critical review of literature data concerning complexing properties of humic substances with actinides relevant for the safety of nuclear waste disposal is thus presented in this work. From these data, two different models have been extracted and speciation diagrams for radionuclides of interest have been calculated in the most representative conditions for natural waters, namely pH range, organics concentration and the presence of competing cations.

### Literature review

Literature data on the conditional formation constants of actinides (tri-, tetra- and hexavalent elements) as well as those of lanthanides (as analogues of trivalent actinides) with humic substances (humic/fulvic acids) are reported in the tables presented in the appendix. No data for pentavalent actinides are reported because of the absence of formation constants in the literature for this oxidation state. Most of the results have been interpreted as the formation of 1:1 (and 1:2) complexes where the organic ligand is a complexing site. In some cases, formation constants have been extrapolated from the Scatchard model [5] (case of uranium) which distinguishes weak from strong sites without any assumptions on their chemical nature. Considering the polyfunctional nature of humic substances (multiplicity of complexing sites), overall formation constants are determined except when humic substances have been simulated as an association of different monomeric units having specific formation constants [6]. Furthermore, as emphasized by many authors [2, 7], the term *interaction constant* instead of formation or stability constant is suggested as more appropriate due to the fact that the determination of formation (or stability) constants in a thermodynamic sense is impossible to perform [8]. Another major problem raising from the determination of interaction constants is the estimation of the ligand concentration: in terms of humic substances weight (g/l), or molarity (moles/l) or expressed as a functional group content (equivalent/l) derived from the total proton capacity or from the carboxylic group content or from the complexing capacity. In the latter case, the complexing capacity represents the maximal number of moles of cations bound to humic substances per gram of humic substances.

Concerning the effect of pH on the interaction constants, much confusion remains between different works. In some cases, the interaction constants appear insensitive to pH [9–10] (as shown for trivalent el-

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ements) and, in other cases, a significant dependence is found [1] (for tri-, tetra- and hexavalent elements). Norden *et al.* [11] have stressed this trend by studying two different techniques (ion-exchange and ultrafiltration) and have shown that this pH influence is related to the experimental techniques. Furthermore, all authors agree with the fact that the complexing capacities are sensitive to pH. These features have been observed in an acidic-neutral pH range (3–7), but above pH 7 the behaviour of interaction constants remain uncertain and some discrepancies between scarce published data exist. A six log unit difference is observed between the values of Bidoglio *et al.* [19] and Maes *et al.* [7] at pH 8.5–9.

Concerning the effect of ionic strength, data are rather sparse and not quite well understood. From literature data [9, 12] interaction constants appear independent of ionic strength whereas the complexing capacities seem to depend on it.

As seen from the appendix, numerous data are available for trivalent elements in similar conditions of pH and ionic strength. Some discrepancies exist between the data (three orders of magnitude in  $\log \beta$ ) obtained in the same pH range (4–7) which are until now unexplained. However, differences in the analytical techniques and experimental conditions (different cation concentrations) may be a reason of these disagreements. In the case of tetravalent and hexavalent elements, literature data appear rather scattered and sparse. In these conditions, a straightforward comparison of data is not reasonable. Nevertheless, some comments should be pointed out as the non difference observed between the interaction constants of U(IV) and U(VI) from the work of Li *et al.* [37] and the differences between the interaction constants of U(IV) and Th(IV) (3 to 6 orders of magnitude) (see appendix).

Since actinides exist in several oxidation states (III, IV, V or VI), we selected in this work elements representative for each oxidation state: americium, thorium and uranium respectively for the tri-, tetra- and hexavalent elements. This choice was based upon the fact that i) numerous data exist for these elements ii) these cations will not be reduced by humic substances.

From the appendix, two different models for determining the interaction constants have been selected. The first one refers to Choppin's work [1], the second one to a single site model as explained below. In Choppin's complexation model, the results have been interpreted as the formation of 1:1 and 1:2 complexes where the ligand is supposed to be a carboxylic site. Interaction constants are dependent on pH (a linear relationship up to pH 7) as well as the ligand concentration (the pH-dependancy is related to the ionization degree of humic substances). It should be mentioned that the interaction constants have been determined in trace concentrations of radioelements and in a relatively narrow pH range (3.5–5.7). Therefore, values used at higher pH are extrapolated and no experimental verification has still been made. Thus, this will constitute a limitation of this model. Table 1

**Table 1.** Interaction constants values for the Am(III), Th(IV) and U(VI)-humic substances systems in the case of Choppin's model at a ionic strength of 0.1 M NaClO<sub>4</sub> and pCO<sub>2</sub> = 10<sup>-3.5</sup> atm.  $\alpha$ , the degree of dissociation, is calculated from pH = pK<sub>a</sub> + log(x/1 - x) and [COOH] = 3.86 meq/g

	Am(III)	Th(IV)	U(VI)
$\log \beta_1$ (l/mol)	3.8 + 10.6 $\alpha$	9.2 + 7.1 $\alpha$	5.0 + 4.8 $\alpha$
$\log \beta_2$ (l <sup>2</sup> /mol <sup>2</sup> )	10.4 + 5.3 $\alpha$	14.2 + 7.6 $\alpha$	8.5 + 4.5 $\alpha$

**Table 2.** Interaction constants and complexing capacities values for the Am(III) and U(VI)-humic substances systems in the case of single site model at a ionic strength of 0.1 M NaClO<sub>4</sub> and pCO<sub>2</sub> = 10<sup>-3.5</sup> atm

	Am(III)	U(VI)
$\log \beta_1$ (l/mol)	6.0 < $\log \beta_1$ < 8.5	6.5 < $\log \beta_1$ < 7.4
$W$ (mmol/g)	0.1 < $W$ < 1.2 <sub>(FA)</sub> 0.1 < $W$ < 1.5 <sub>(HA)</sub>	0.2 < $W$ < 1.0

summarizes the interaction constants used in this work for Am(III), Th(IV) and U(VI).

In the single site model, minimum and maximum values (Table 2) have been selected for the interaction constants ( $\log \beta$ ) of Am(III) and U(VI) and the complexing capacities ( $W$ ) of the organic ligands. For Am(III), a pH limit has been set for the selection of data. Only values at pH > 4 have been used (for the minimum  $W$  values of humic and fulvic acids, considering the small difference between the  $W$  values (0.07 and 0.1) a common data has been taken (0.1)). For U(VI), only the strong complexing sites have been considered. In the single site model, the interaction constants are supposed to be invariant with pH (based on the results obtained in the previous works on trivalent cations [9–10] in the pH range 4–7) as well as the complexing capacities. This latter assumption constitutes a limitation of this model since pH-dependancy has been observed, but it will be a penalizing assumption. Another limitation comes from the lack of data at higher pH which makes the extrapolation of the independency of  $\log \beta$  with pH uncertain (as for the Choppin's model). Furthermore, no assumption on the chemical nature of the ligand (a complexing site) is made, and only complexes of 1:1 stoichiometry are considered. These different assumptions lead to a different approach compared to the previous model described above.

## Results and discussion

All the speciation calculations for the radioelements have been made by considering the following reac-

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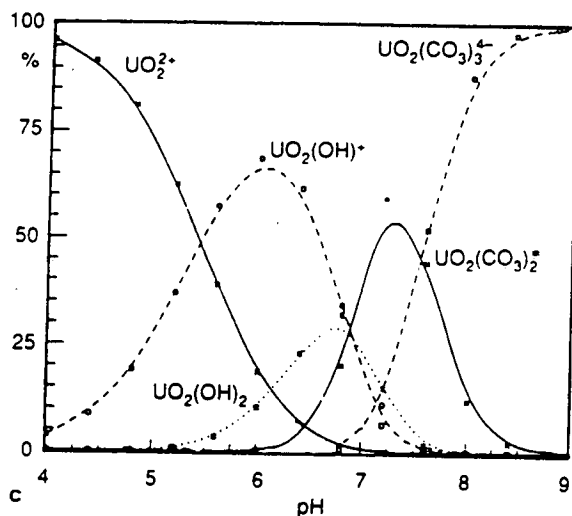
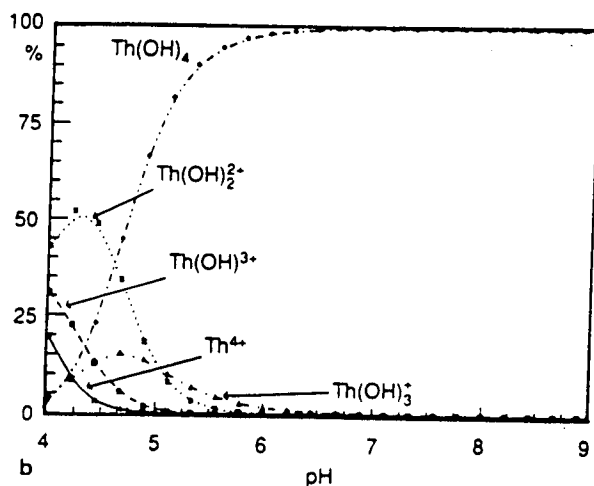
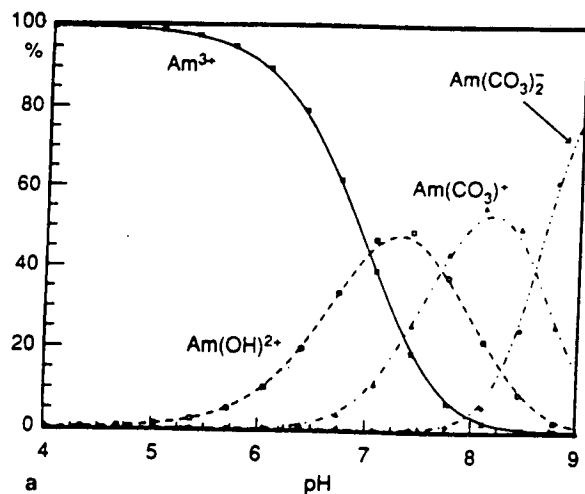


Fig. 1. Species distribution plot for Am(III), Th(IV) and U(VI) in the inorganic system OH/CO<sub>3</sub> at a ionic strength of 0.1 M NaClO<sub>4</sub> and pCO<sub>2</sub> = 10<sup>-3.5</sup> atm. No polynuclear species have been taken into account for Th(IV) and U(VI). Curves were not drawn when species concentration was inferior to 15%.

tions: hydrolysis, carbonate and organic complexation, assuming that the hydroxide and carbonate ions are the major inorganic ligands found in natural waters. A constant ionic strength *I* of 0.1 M and a

Table 3. Interaction constants for Am(III), Th(IV) and U(VI) at a ionic strength of 0.1 M NaClO<sub>4</sub>.

Complex	Am	Th	U
<b>OH*</b>			
M(OH)	-7.4	-3.8	-5.4
M(OH) <sub>2</sub>	-15.3	-7.7	-12.3
M(OH) <sub>3</sub>	-24.3	-12.7	-20.0
M(OH) <sub>4</sub>	-	-16.9	-
<b>CO<sub>3</sub>**</b>			
M(CO <sub>3</sub> )	6.3	-	8.2
M(CO <sub>3</sub> ) <sub>2</sub>	10.1	-	15.9
M(CO <sub>3</sub> ) <sub>3</sub>	11.3	-	21.8
	[13]	[14]	[15]

\*  $M^{n+} + iH_2O \rightleftharpoons M(OH)_i^{(n-i)+} + iH^+$

\*\*  $M^{n+} + iCO_3^{2-} \rightleftharpoons M(CO_3)_i^{(n-2i)+}$

pH range of 4–9 have been considered. The humic substances concentration range varies from 0.1 to 10 mg/l. This range is representative for groundwaters of crystalline rock formation (granitic) [4]. It should be pointed out that higher concentrations could be found in surface waters or groundwaters from sedimentary formations [4].

The speciation of Am(III), Th(IV) and U(VI) in the inorganic system is presented on the Fig. 1 using data of Table 3. Under atmospheric conditions, hydroxide and carbonate complexes are present for Am(III) and U(VI), whereas for Th(IV), hydrolysis is the only phenomena occurring in the whole pH range, considering that no carbonate complexes should be formed as stressed by Lieser *et al.* [48].

#### Actinide speciation in the absence of competing cations

The actinide speciation of Am(III), Th(IV) and U(VI) in the presence of humic substances (HS) has been calculated by using the interaction constants given in Tables 1 and 2 in the case of Choppin's model and single site model respectively. For a more comprehensive presentation, only speciation curves obtained for U(VI) will be reported. Some species distribution plots of Am(III) in the conditions specified above could be found in a previous work [16]. In the further discussion, the term humate will be used for humic and fulvic acids except in some cases which will be specified.

In the case of *Choppin's model*, humate complexation appears as the major reaction occurring between pH 4 and 7–7.5 for U(VI) depending on the humic concentration (0.1–10 mg/l) as shown on Fig. 2. For higher pH, carbonate complexes become predominant. For Am(III), humic substances complexes are predominant between pH 4 and 9 for the lowest humic concentration (0.1 mg/l) as already shown in a pre-

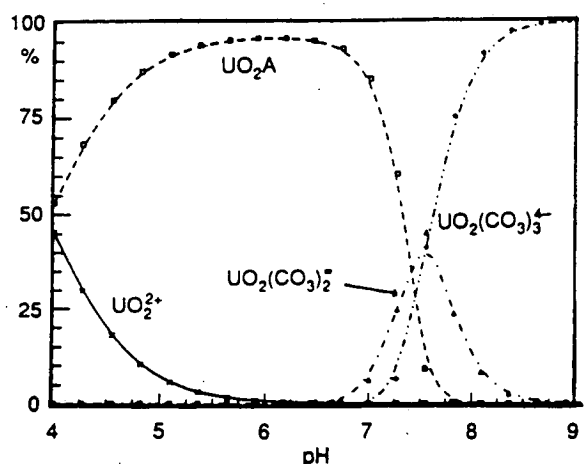


Fig. 2. Species distribution plot for the U(VI)-OH-CO<sub>3</sub>-humic substances system by using Choppin's model at a ionic strength of 0.1 M NaClO<sub>4</sub>, pCO<sub>2</sub> = 10<sup>-3.5</sup> atm and [humic substances] = 0.1 mg/l. A represents the organic ligand. Charges of organic species have been omitted. Curves were not drawn when species concentration was inferior to 15%.

vious work [16]. In the case of thorium, organic complexes are the major species up to pH 6.5 for 0.1 mg/l of humic substances, and up to pH 7.5 for 10 mg/l. Beyond these pH values, Th speciation is entirely dominated by hydrolysis.

In the case of the *single site model*, the use of the minimum values for the interaction constants and the complexing capacities (Table 2) leads to an absence of organic complexation at the lowest concentration of humic materials (0.1 mg/l). The speciation curves for Am(III) and U(VI) are similar to those presented for the inorganic system (Fig. 1). Considering these results, we determined the minimal concentrations of humic substances to have the predominance of the organic complexes at a given pH (pH 5–6) as reported in Table 4. The organic complexes become the dominating species above 10 and 3 mg/l of humic substances, in the case of americium and uranium respectively. The same calculations have been made by taking the highest interaction constants values and the lowest complexing capacities (as a restricting parameter). Results are given in Table 4. Organic complexation will occur as a major reaction for very low humic substances concentrations (0.03 mg/l for Am(III) and 0.2 mg/l for U(VI)).

By using the maximum values for the interaction constants and complexing capacities (Table 2), organic complexation is the major reaction occurring up to pH 8 for Am(III), and up to pH 5.5 or 7 for U(VI) at 0.1 mg/l or 10 mg/l of humic substances respectively (as shown on Fig. 3).

#### Actinide speciation in the presence of competing cations

In order to be more representative of natural waters conditions, speciation calculations have been

Table 4. Minimal humic substances concentrations values to have organic complexes as major species as a function of interaction constants and complexing capacities values (single site model) for Am(III) and U(VI) in the absence or presence of a competing cation (Ca, Al)

	Am(III) pH 6	U(VI) pH 5
$\log \beta_{1\min}$ (l/mol)	6.0	6.5
$W$ (mmol/g)	0.1	0.2
$[HA]_{\min}$ (ppm)	10 <sup>a</sup> /32 <sup>b</sup> /95 <sup>c</sup> 55 <sup>d</sup>	2.6 <sup>a</sup> /5 <sup>b</sup> /10 <sup>c</sup>
$\log \beta_{1\max}$ (l/mol)	8.5	7.4
$W$ (mmol/g)	0.1	0.2
$[HA]_{\min}$ (ppm)	0.03 <sup>a</sup> /0.1 <sup>b</sup> /1.7 <sup>c</sup>	0.2 <sup>a</sup> /0.6 <sup>b</sup> /1.3 <sup>c</sup>

<sup>a</sup> Without any competing cation

<sup>b</sup> In the presence of Ca (10<sup>-3</sup> M)

<sup>c</sup> In the presence of Al (10<sup>-5</sup> M) at pH 4

<sup>d</sup> In the presence of Al (10<sup>-5</sup> M) at pH 5.

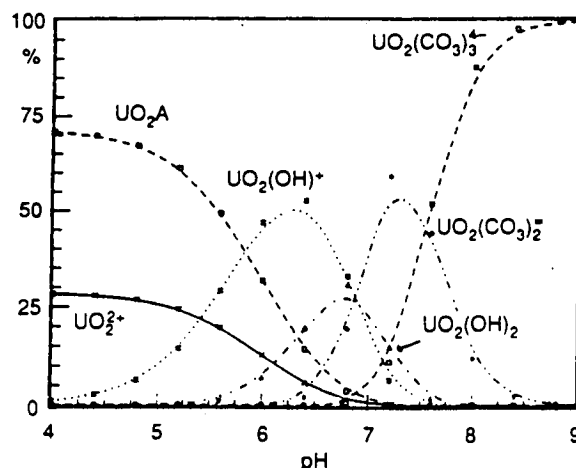


Fig. 3. Species distribution plot for the U(VI)-OH-CO<sub>3</sub>-humic substances system by using the maximum values of the single site model ( $\log \beta_1 = 7.4$  and  $W = 1.0$  mmol/g) at a ionic strength of 0.1 M NaClO<sub>4</sub>, pCO<sub>2</sub> = 10<sup>-3.5</sup> atm and [humic substances] = 0.1 mg/l. Charges of organic species have been omitted. Curves were not drawn when species concentration was inferior to 15%.

performed by taking into account the competition with cations present in natural waters. This competition effect will only occur if the complexing sites are the same for these cations and the radioelements under investigation. This assumption is debated in the literature: it has been shown by different authors that the presence of calcium did not affect i) the complexation of copper (10<sup>-9</sup> to 2 · 10<sup>-7</sup> M) by humic substances (0.3 mg/l) at pH 8.2 even in the presence of 0.01 M of calcium [17] ii) the kinetics of copper complexation

by humic substances whereas the kinetics of copper complexation by EDTA is affected in its presence [18] iii) the terbium complexation by humic acids at pH 5.5 and 8.5 [19]. From these results, the possible existence of different sites according to the different cations has been proposed [17–19]. In our calculations we will assume a competition effect (presence of same sites of complexation) with calcium and aluminium selected as representative of cations found under in-situ conditions in natural waters. In the case of calcium, a competition with trivalent elements has been observed for calcium concentrations starting from 0.01 M as described in [10]. Iron has not been retained for this study due to the oxidoreduction phenomena occurring with humic substances [20].

Interaction constants values selected for Ca(II), Al(III)-humic substances systems are  $\log\beta(\text{Ca}) = 3.3$  and  $\log\beta(\text{Al}) = 6.8$  (from values given in the appendix). In this case, no model has been considered since no data are available in the literature. The pH independency of  $\log\beta$  for Ca(II) and Al(III) is assumed. As a competition effect is supposed to exist, the ligand concentration is supposed to be the same as for the actinide/lanthanide system. The concentration ranges for Ca and Al used in our simulations are:  $10^{-5} < [\text{Ca}] < 10^{-3}$  M and  $[\text{Al}] < 10^{-5}$  M. These values represent the mean concentration ranges found in natural waters for both elements [21]. Furthermore, in our speciation calculations, we will neglect i) the formation of polynuclear and colloidal species in particular for aluminium ii) the flocculation phenomena which could occur at relatively high concentrations of cations and leading to insoluble phases [22].

#### Presence of calcium

In the case of *Choppin's model*, the presence of calcium at  $10^{-3}$  M slightly affect the U(VI) speciation in the pH range 4–4.5 (as shown on Fig. 4a). No effect of the presence of calcium, even at  $10^{-3}$  M, is observed on the speciation of Am(III) and Th(IV) at 0.1 ppm of humic substances.

In the case of *the single site model*, the minimal humic acid concentration to have predominance of the organic complexes in the presence of the competing cation has been determined (Table 3). The presence of a competing cation increases the minimal humic acid concentration to have organic complexes as major species, in particular for Am(III) when the minimum values are considered. In other cases, the humic concentrations remain representative of concentrations found in ground natural waters (crystalline formation).

#### Presence of aluminium

In the case of *Choppin's model*, a slight effect of the presence of aluminium is observed on the speciation of Am(III) and U(VI) (Figure 4b) between pH 4 and 5 only at low humic acid concentration (0.1 mg/l). In

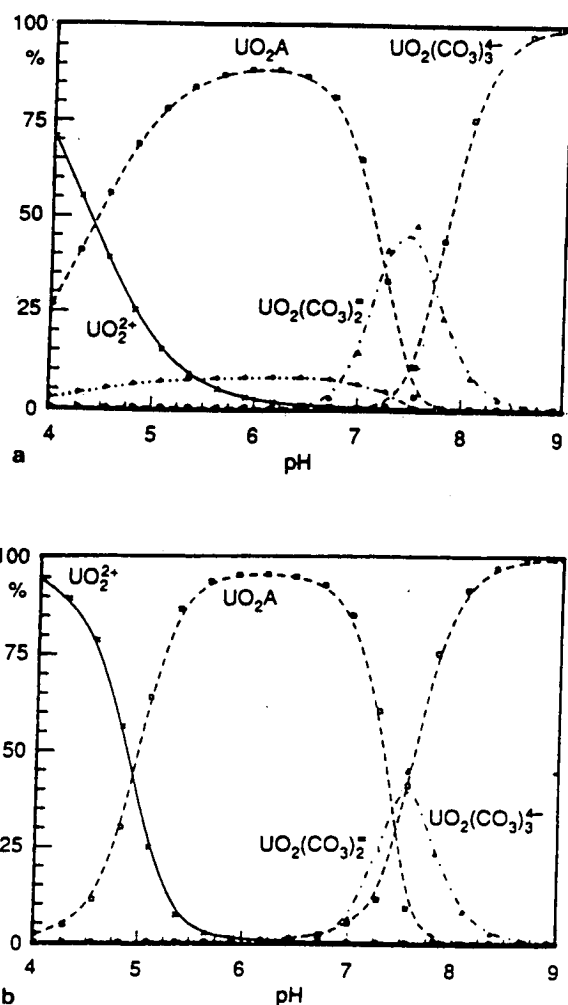


Fig. 4. Species distribution plot for the U(VI)–OH–CO<sub>3</sub>–humic substances system by using the Choppin's model in the presence of a competing cation at a ionic strength of 0.1 M NaClO<sub>4</sub>,  $p\text{CO}_2 = 10^{-3.5}$  atm and [humic substances] = 0.1 mg/l. 4a-[Ca] =  $10^{-3}$  M; 4b-[Al] =  $10^{-5}$  M. Charges of organic species have been omitted. Curves were not drawn when species concentration was inferior to 15%.

the case of thorium, a competitive effect occurs below pH 7: at low humic concentration (0.1 mg/l), only hydrolysed species are present, whereas at higher concentrations (10 ppm) organic complexes are predominant up to pH 6 (instead of 7.5 in the absence of Al).

In the case of *the single site model*, as for calcium, minimal humate concentrations have been determined to have organic complexation as a major phenomena (Table 4). Compared with calcium, these minimal concentrations are higher for aluminium. The effect is particularly marked in the case of Am(III) with the minimal values.

#### Conclusions

The investigation of the role of humic substances on the behaviour of radioelements through speciation cal-

culations show that humic substances may strongly influence the chemical species of radionuclides in natural waters conditions. The use of two different models (of which the major difference comes from the dependence or independence of the interaction constants and complexing capacities of the organic ligands) leads to relatively similar conclusions, namely organic complexation dominates radioelement speciation up to pH 7 (or even 8) for humic substances concentrations found in natural waters (as low as 0.1 mg/l). Above this pH value inorganic complexes become predominant. Nevertheless, experimental verification of the extrapolation of interaction constants at higher pH (pH > 7) should be undertaken. In the presence of competing cations the speciation of radioelements may be affected. The presence of calcium modifies their speciation, only at high calcium concentration (40 mg/l or  $10^{-3}$  M), in a relatively narrow pH range (4–6 for Am(III) and 4–5 for U(VI)) except for Th(IV) for which no influence is observed. The effects of aluminium are somewhat more important on radioelement speciation: at 0.1 mg/l of humic substances and [Al]  $10^{-5}$  M, organic complexation will be a minor phenomena in a pH range 4–5. It should be stressed that, in these calculations, neither colloid formation of radionuclides or competing cations has been taken into account for the formation of mixed complexes (with carbonate or hydroxyde) at higher pH.

In order to assess these conclusions, further experimental studies on the complexing behaviour of humic substances should be performed, in particular the effect of pH in a neutral-basic range and the effect of ionic strength.

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## Appendix

### Notations

- I ionic strength  
M cation  
HA, FA humic, fulvic acid  
A humic or fulvic ligand (a molecule or a site according to the authors)  
 $\alpha$  dissociation coefficient of humic substances  
 $\beta_1$  interaction constant related to the following equilibrium:  

$$\text{M} + \text{A} = \text{MA} \quad \text{with} \quad \beta_1 = [\text{MA}]/[\text{M}][\text{A}]$$
 $\beta_2$  interaction constant related to the following equilibrium:  

$$\text{M} + 2\text{A} = \text{MA}_2 \quad \text{with} \quad \beta_2 = [\text{MA}_2]/[\text{M}][\text{A}]^2$$

The unit of the constants  $\beta_1$  and  $\beta_2$  will be the opposite of the unit chosen by the author for the humic or fulvic concentration.

Interaction constants have been recalculated in l/g (values in brackets).

### Abbreviation of techniques

- D dialysis  
IE ion-exchange  
LPAS laser photoacoustic spectroscopy  
SE solvent extraction  
SEC size-exclusion chromatography  
SP spectrophotometry  
TI titration  
TRLIS time-resolved laser-induced spectrofluorometry  
TRLFS time-resolved laser fluorescence spectroscopy  
UF ultrafiltration

## Trivalent Lanthanides - Humic Substances

Ligand	Tech.	pH	I	W (mmol/g)	$\log \beta_1$	unit	Ref
<b><u>Eu(III)</u></b>							
HA (Aldrich)	SEC	5	0.02	-	4.3	l/g	23
"	UF	5	0.1	0.28	4.5	l/g	24
"	D	4.5	0.05	0.22	6.2 (2.5)	l/mol	25
	IE	6.0	0.01	-	7.5	l/mol	7
HA (Gorleben)	IE	6.0	0.01	-	8.1	"	7
HA (clay)	IE	6.0	0.01	-	7.5	"	7
HA (lake)	IE	4.5	0.1	-	$\beta_1: 7.4 (4.9)$ $\beta_2: 10.3$	l/eq H <sup>+</sup>	10
"	SE	4-5.5	0.1		$\log \beta_1 = 8.9\sigma + 4.4$ $\log \beta_2 = 3.6\sigma + 11.1$		27
		4.65 ( $\sigma = 0.54$ )		-	$\beta_1: 8.6 (5.7)$ $\beta_2: 13$	l/eq COOH	
FA (sediment)	IE	4.5	0.1	-	6.5 (4.2)	l/eq H <sup>+</sup>	28
FA (river)	IE	4-5	0.1	-	10.3 (7.4)	l/mol (MW~800)	29
HA (soil)	IE	9	0.1	-	13.7 (11.2)	l/eq H <sup>+</sup>	30
HA (Gorleben)	IE	9.0	0.1	-	12.9	"	7
HA (clay)	IE	9.0	0.1	-	13.5	"	7
HA Aldrich)	IE	9.0	0.1	-	13.1	"	7
<b><u>Tb(III)</u></b>							
HA (Gorleben)	LITRS	8.5	0.1	0.75	6.7 (3.6)	l/mol	19



# Trivalent Actinides - Humic Substances

Ligand	Tech.	pH	I	W (mmol/g)	$\log \beta_1$	unit	Ref
<b>Am(III)</b>							
FA (ground water)	SP	4.65	0.1	0.88	6.4 (3.1)	l/mol	31
FA (surface water)	SP	"	"	1.22	6.0 (3.1)	"	31
FA (granitic water)	SP	"	"	0.45	6.5 (3.2)	"	32
"	SEC	5	0.1	-	4.2	l/g	32
HA (granitic water)	SP	4.65	0.1	0.3	7.0 (3.5)	l/mol	32
"	SEC	5	0.1	-	4.6	l/g	32
HA (surface water)	SP	4.65	0.1	1.20	7.0 (4.1)	l/mol	31
HA (Aldrich)	SP	4.65	0.1	0.96	7.0 (4.0)	l/mol	31
	SP	6.0	0.1	1.5	6.4 (4.1)	"	33
	LPAS	6.0	0.1	1.2	6.3	l/mol	9
HA (Gorleben)	SP	6.0	0.1	1.1	6.4 (4.0)	l/mol	33
HA (sediment)	SP	"	"	1.03	7.0 (4.0)	"	31
"	IE	4.5	0.1	-	$\beta_1: 6.8 (4.4)$ $\beta_2: 10.6$	l/eq H <sup>+</sup>	26
"	SE	4-5.5	0.1	-	$\log \beta_1 = 10.6\sigma + 3.8$ $\log \beta_2 = 5.3\sigma + 10.4$		
		4.65 ( $\sigma = 0.54$ )			$\beta_1: 9.3 (6.6)$ $\beta_2: 13.3$	l/eq COOH	27
	SP, UF	5-6	0.1	0.4/1.2	6.4 (3.4/3.9)	l/mol	9
		6	1.0	0.9	6.4 (3.8)	"	9
HA (soil)	IE	6.5	0.1	-	$\beta_1: 6.4 (3.1)$ $\beta_2: 10.6$	l/mol (MW = 1800)	34
<b>Cm(III)</b>							
HA (Aldrich)	LITRS	4	0.1	0.1	8.4 (4.4)	l/mol	12
		5	0.1	1.2	8.5 (5.5)	"	12
		5	0.001	1.6	8.0 (5.2)	"	12
FA (granitic water)		3	0.1	0.02	7.3 (2.6)	"	12
		5	"	0.07	7.8 (3.7)	"	12
HA (Gorleben)	TRLFS	6.0	0.1	1.1	6.2 (3.8)	l/mol	35
<b>Pu(III)</b>							
HA	SE	2.9	0.5	-	2.8 (0.2)	l/eq COOH	36
		5.0	"	-	3.1 (0.7)	"	"

## Tetravalent Actinides - Humic Substances

Ligand	Techn.	pH	I	$\log \beta_1$	$\log \beta_2$	unit	Ref
<u>U(IV)</u>							
HA (soil)	D	6	0.01	7.0* (strong sites: 0.5mmol/g) 4.5* (weak sites: 4.5 mmol/g)		l/g	37
FA (soil)	D	6	0.01	6.6* (strong sites: 0.3mmol/g) 4.9* (weak sites: 1.8mmol/g)		l/g	37
<u>Th(IV)</u>							
HA (sediment)	SE	5.00 ( $\sigma=0.54$ )	0.1	13.2 (10.4)	18.4 (12.8)	l/eq H <sup>+</sup>	38
FA (soil)	SE	5.00 ( $\sigma=0.8$ )	0.1	10.8 (8.2)	15.04 (9.8)	l/eq H <sup>+</sup>	38
	SE	4.00 ( $\sigma=0.7$ )	0.1	9.8 (7.1)	13.5 (8.2)	"	38
HA (Aldrich)	SE	4.00 ( $\sigma=0.40$ )	0.1	11.0 (8.2)	16.4 (10.9)	l/eq H <sup>+</sup>	38
HA (sediment)	SE		0.1	9.2+7.1 $\sigma$	14.2+7.6 $\sigma$	l/eq COOH	1
HA (Aldrich)	SEC	5.0	0.02	15.6	-	l/g	23
<u>Pu(IV)**</u>							
HA (sediment)	SE		0.1	9.8+9 $\sigma$	16.0+9 $\sigma$	l/eq COOH	1

\* constants associated with Scatchard model (two types of sites)

\*\* estimated constants [1]

# Hexavalent Actinides - Humic Substances

Ligand	Tech.	pH	I	$\log \beta_1$	$\log \beta_2$	unit	Ref
HA (sediment)	SE		0.1	$5.0+4.8\sigma$	$8.5+4.5\sigma$	l/eq COOH	1
HA (Aldrich)	IE	4.0 ( $\sigma=0.47$ )	0.1	5.1 (2.4)	8.9 (3.5)	l/eq H <sup>+</sup>	39
	IE	4.5	0.1	6.5-7.4 (W = 0.2mmol/g)	-	l/mol	40
	SEC	5.0	0.02	4.4	-	l/g	23
HA (soil)	D	6.0	0.1	6.7* (strong sites: 1.0mmol/g) 4.7* (weak sites: 9.5mmol/g)		l/g	37
FA (soil)	"	6.0	0.1	7.4* (strong sites: 0.2mmol/g) 5.6* (weak sites: 3.8mmol/g)		l/g	37
HA (peat)	Ti	3.5-7	0.1	7.8	-	?	41
HA (sea)	Ti	4.0	0.1	5.0	8.5	?	42
FA (sea)	"	"	"	4.5	9.3	?	42

\* constants associated with Scatchard model (two types of sites)

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## Ca(II) - Humic Substances

Ligand	Tech.	pH	I	$\log \beta_1$	unité	Ref.
HA (Aldrich)	SE	5.01 ( $\alpha=0.65$ ) 3.88 ( $\alpha=0.44$ )	0.1	3.32 (0.94) 2.25 (-0.13)	l/eq H <sup>+</sup>	43
HA (surface water)	Ti	8.2	0.1	6.0* (1.7) 4.1* (0.4) 2.9* (0.16)	l/mol	17
HA (sediment)	Ti	3-5	0.1-0.01	7.2**	?	44

\* interaction constants associated to a discrete model (three types of sites)

\*\* intrinsic constant

## Fe(III), Al(III) - Humic Substances

Ligand	Tech.	pH	I	W (mmol/g)	$\log \beta_1$	unit	Ref
<u>Al(III)</u> HA (sediment)	D	3-5	0.1-0.01	-	3.4-3.8* (Al <sup>3+</sup> ) 4.4-5.6§⊙ (AlOH <sup>2+</sup> )	?	45
HA (Aldrich)	IE	3-5	-	0.1-0.4	6.8** (2.8-3.4)	l/mol	46
Natural water	IE	-	-	1-3***			46
<u>Fe(III)</u> FA (soil)	SP	1.0-2.5	0.1	-	4.2-4.5 (1.2-1.6)	l/mol (MW=900)	47

\* intrinsic constants

\*\* constants associated with Scatchard and Langmuir model \*\*\* mmoles/g DOC (dissolved organic carbon)

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